HETEROGENEOUS CATALYSIS IN POLYMOLECULAR ADSORPTION LAYERS

-USSR-

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[Following is the translation of an article by V. I. Gol'-
danskiy, Academician N. N. Semenov, and N. M. Chirkov
entitled "Geterogennyy kataliz v polimolekulyarnykh adsor-
bitsionnykh sloyakh" (English version above) in Doklady
Akademii Nauk SSSR (Reports of the Academy of Sciences USSR),
Vol LII, No 9, Moscow, 1946, pages 783-785.]

All contemporary theories of heterogeneous catalysis refer to
the phenomena connected with the filling or non-filling of the mono-
molecular adsorption layer on the surface of the catalyst with rea-
ctive molecules.

Moreover, many vapors at suitable pressures $P/P_{sat} > 0.5$
(P = vapor pressure, P_{sat} = saturation pressure of the vapor at the
temperature of the experiment) begin to be adsorbed on the surface
and form polumolecular layers, whose thickness at $P/P_{sat} = 0.8-0.9$
reaches a magnitude of the order of tens of molecular layers, and
at P/P_{sat} tending to unity, it is of the order of hundreds of mole-
cular layers. Such a polymolecular adsorption film, of a thickness
from several units to tens of monolayers, should be similar to a
liquid as far as its properties are concerned. Therefore, one may
assume that all the substances which catalyze some reaction in the
liquid phase shall also catalyze this reaction in the above mentioned
polymolecular adsorption film.

Thus, if in the gaseous or vapor phase at $P/P_{sat} > 0.5$ one
should place an inert solid surface, on which there are traces of
compounds catalyzing a liquid phase reaction, then having all the
properties of a liquid, such a surface shall display the properties
of heterogeneous catalyst because of a higher velocity of reaction
in the polymolecular adsorption film, being comparable to a reaction
in the vapor phase. Such a simplified concept of heterogeneous catal-
ysis, as far as we know, has never been experimentally verified.

In order to demonstrate its existence we have chosen an ester-

ification reaction (the production of ethyl acetate from acetic acid and ethanol) and the hydrolysis of the ethyl acetate, which reactions, as is known, are catalyzed in the liquid phase by acids, for example, by hydrochloric acid HCl. As Ostwald and Arrhenius have shown, the catalytic activity of acids in many liquid-phase reactions is the function of the hydrogen ion H^+ (or the solvated hydrogen ion, for example, OH_3^+), and the velocity of such reactions is proportional to the electrical conductivity of the solution and is dependent on the nature of the acid-catalyst.

In previous information (1) we have shown that the surface electrical conductivity of dielectrics which may be imagined to be a polymolecular water film, at constant conditions, there are present on the surface electrolytes which often dissolve in the water film. In other words, the surface electrical conductivity has purely an electrolytic character. In water vapor and hydrochloric acid on the surface of quartz, mica, etc., there forms a conducting layer whose electrical conductivity depends on P/P_{sat} according to the formula $\sigma = \sigma_0 e^{\alpha P/P_{sat}}$, where α is found to be of the order of 10-15 (for example, for quartz $\alpha = 11.0$).

Because of that, it was natural to assume that the ions H^+ shall catalyze the reaction of esterification and hydrolysis in the surface polymolecular adsorption layer, and we shall show the heterogeneous catalysis of a surface (for example, a glass one) in the vapors of a mixture of water, hydrochloric acid, acetic acid and ethanol.

Such experiments were conducted by us in mixtures of ethanol vapors, acetic and hydrochloric acids (esterification), water, hydrochloric acid and ethyl acetate (hydrolysis), while keeping the HCl in the vapor phase between 0.6 and 18% at total pressures of 56-336 mm Hg and temperatures of 45-82° C. The magnitude P_{sat} was determined according to the dew point for the given mixture composition and known temperature. The experiments were conducted in a 1.5 liter glass vessel. The magnitude of the glass surface changed by filling the vessel with wide glass tubes. Thus, the ratio of surface to volume $S/V_{relative}$ could be increased up to 8.8 (in empty vessels $S/V_{rel} = 1$). The rate of reaction has proved to be proportional to the glass surface. This shows that the reaction proceeds solely on the surface and not in the bulk. In the preliminary stage (30-40% conversion) the reaction may be satisfactorily expressed by an equation of zero order.

The equilibrium in the case of equimolecular mixture is found in the conditions of our experiments for 92% esterification, at the time when in the liquid phase for analogous conditions the equilibrium is at 66% esterification. The reaction rate is not defined by an absolute pressure magnitude, but by the ratio P/P_{sat}, and the rate dependence on the pressure is expressed as follows: $\omega = \omega_0 e^{\beta P/P_{sat}}$,

where it is found that $\beta \cong 11.6$, which is close to the value
of the existing coefficient for the surface electrical conductiv-
ity. The reaction rate increases on addition of HCl into the bulk.
If one compares the esterification reaction rate at different tem-
peratures, but for constant P/P_{sat}, the obtained dependence on tem-
perature well satisfies the Arrhenius equation; where the activa-
tion energy $E = 15,000 \pm 500$ cal/mole (also the comparison velocity
at different temperatures and equal total pressures P gives in the
given case a negative temperature coefficient because the fall of
P/P_{sat} with the increase in temperature effects more strongly than
the temperature acceleration of rate on the calculation of energy
of activation).

For the reaction in the liquid phase, as regards an acid
catalyst, $E = 16,300$ cal/mole. One may therefore claim that a poly-
molecular heterogeneous catalytic reaction in the liquid phase has
an identical temperature coefficient.

All these results directly confirm the announced thesis at the
beginning on the existence of a polymolecular heterogeneous catalysis.
The hydrogen ions being homogeneous catalysts of the reaction in the
liquid phase are also the reason for the heterogeneous catalysis of
the surface in reactions in the vapor phase. We assume that not
only ionic catalysts may play such a role. Many reactions in the
liquid phase are catalyzed, for example, by mercury salts or copper
salts with complex ion formation. One may expect the presence of a
catalytic effect of these combinations also in the case of the poly-
molecular heterogeneous catalysis.

We also believe that the very wide application of a catalyst
of the type of phosphoric acid H_3PO_4 functions in the fashion of poly-
molecular heterogeneous catalysis.

The main point is that phosphoric acid is a very good water
absorbent, i.e., it strongly lowers P_{sat}. Because of this, also at
high temperature and comparatively small absolute pressure P, the
ratio P/P_{sat} may be of importance, meanwhile this quantity is regarded
as the fundamental criterion, defining the thickness of the adsorption
film, the surface electric conductivity, and finally the rate of
the polymolecular heterogeneous catalytic reaction. Thus we have the
right to expect here the formation of adsorbing water films and other
reagents and the incidence of many reactions in such a concentrated
polymolecular solution of phosphorous acid. Further experiments
show how widespread the class of polymolecular heterogeneous cataly-
tic reactions is.

One should note that the structure of the problem as presented
here, and the results of the esterification experiments and of hydrol-
ysys are also of interest for the basic comparison of the reaction
kinetics in the gaseous and liquid phases respectively.

Although the ionization under normal conditions is impossible

the gaseous phase, ionic (in the liquid phase) reactions may take place in vapors or gases only with the aid of the polymolecular heterogeneous catalyst, but not homogeneously. This has been qualitatively proved in the works of Hinshelwood (1) and Bell (3). Non-ionic simple and chain reactions may take place in the liquid phase as well as homogeneously in the vapor phase. Thus, comparative studies on reaction rates in the vapor and liquid phases may serve to define the reaction type.

The experimental portion of this work shall soon be published in detail.

Received, 28 May 1946.

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